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IAEA THORIUM GAMMA-RAY CALIBRATION MATERIAL: APPLICATION OF HIGH RESOLUTION SPECTROMETRY TO MONITOR THORIUM/URANIUM RATIO

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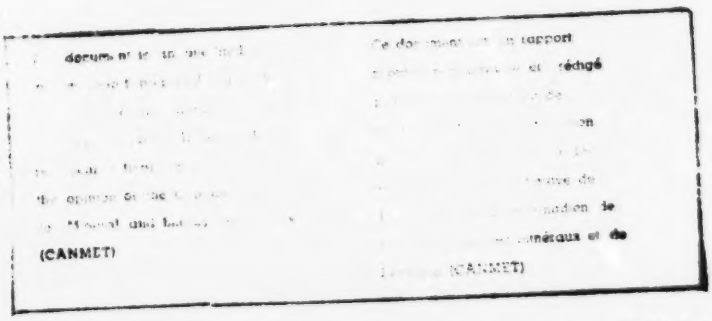

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IAEA THORIUM GAMMA-RAY CALIBRATION MATERIAL: APPLICATION OF HIGH RESOLUTION SPECTROMETRY TO MONITOR THORIUM/URANIUM RATIO

by

C.W. Smith* and R.L. Grasty**

ABSTRACT

A technique was developed for rapid measurement of the equivalent thorium to equivalent uranium ratio of thorium-rich material.

High resolution gamma-ray spectrometry was used to measure the ^{208}Tl to ^{214}Bi activity ratio from the relative intensities of their corresponding photopeaks at 583 and 609 KeV. Owing to the proximity of the energy of these emissions, the intensity ratio was independent of variations in the geometry and absorption properties of the sample.

The procedure was applied to test rock samples collected from a britholite vein associated with the Oka, Quebec Carbonatite for suitability as source material for an IAEA interlaboratory gamma-ray thorium standard, which was required to have a minimum equivalent thorium to equivalent uranium ratio of about 100. Following crushing to approximately -100 mesh equivalent uranium and thorium were measured by gamma-ray spectrometry and found to be 0.0283 ± 0.0007% and 2.74 ± 0.06% respectively thereby meeting the IAEA requirements.

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ÉTALONNAGE AIEA DU MATÉRIEL À PARTIR DU RAYONNEMENT GAMMA DU THORIUM APPLICATION DE LA SPECTROMÉTRIE À HAUTE RÉSOLUTION POUR LA DÉTERMINATION DU RAPPORT THORIUM-URANIUM

par

C.W. Smith* et R.L. Grasty**

RÉSUMÉ

On a mis au point une technique de mesure rapide de l'équivalent thorium à l'équivalent uranium dans un matériel riche en thorium.

On a utilisé la spectrométrie à rayonnement gamma à haute résolution pour mesurer le rapport d'activité du ^{208}Tl au ^{214}Bi à partir de l'intensité de leur pic photométrique respectif, soit 583 et 609 KeV. En raison de la proximité de ces deux émissions énergétiques, le rapport d'intensité était indépendant des variations de la géométrie et des propriétés d'absorption de l'échantillon.

La méthode a été utilisée pour étalonner des échantillons de roche extraits du filon de britholite d'un gîte exploité par la Quebec Carbonatite à Oka afin de déterminer une substance source à rayonnement gamma pouvant être utilisée comme norme inter-laboratoires de l'AIEA pour l'étalonnage du matériel à partir du rayonnement gamma du thorium, laquelle devait comprendre un rapport minimal de l'équivalent uranium à l'équivalent thorium d'environ 100. Suite à un broyage à la maille -200 approximativement, l'équivalent uranium et l'équivalent thorium ont été mesurés à l'aide de la spectrométrie à rayonnement gamma et s'élevaient respectivement à 0,0283 ± 0,0007 % et 2,74 ± 0,06 % conformément aux exigences de l'AIEA.

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INTRODUCTION

Gamma-ray spectrometry is used extensively in the laboratory to measure the radioactivity of both powdered rock and ore samples. The significant contributors of natural gamma-ray emission are potassium-40 and the decay products of uranium-238 and thorium-232. To achieve high sensitivity many laboratories use sodium-iodide crystal scintillation detectors. However, owing to Compton scatter and the limited resolution of sodium iodide detectors, spectral stripping or deconvolution is required to accurately measure the relative contributions of parent isotopes (1).

In order to calibrate the spectrometer, accurately known potassium, uranium and thorium standards must be prepared. Ideally, these standards should be pure in their respective radio-elements. Primary potassium standards are normally made by mixing a pure potassium salt with a radioactively inert matrix such as silica sand. In the case of uranium and thorium, the majority of laboratories rely on certified standard rock samples, such as those produced by the U.S. Department of Energy, New Brunswick Laboratory (NBL) (2,3). These standards, however, were analysed chemically for uranium and thorium, and for use as laboratory gamma-ray standards their state of radioactive equilibrium must be known*. Canadian Certified Reference Materials Project (CCRMP) uranium ores have recently been shown to be essentially in secular equilibrium with respect to the uranium decay series, and several of these also have very high uranium/thorium ratios (4). Secular equilibrium is re-established in much shorter order (≈40y) in the thorium decay series, and most natural rock materials may be assumed to be in radioactive equilibrium. Unfortunately, most natural thorium ores, e.g. monazites, usually have sufficient uranium and associated decay products that they are not ideal as reference materials. Chemical thorium compounds that are in radioactive equilibrium are both rare and costly.

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*Gamma-ray spectrometry values for uranium and thorium concentration are termed equivalent uranium (eU) and equivalent thorium (eTh) to emphasize that radioactive equilibrium between the parent nuclei and their measured decay products is implicity assumed.

In December 1983, the International Atomic Energy Agency held a consultants meeting to discuss the preparation and distribution of suitable laboratory gamma-ray calibration materials for eU and eTh (5). Five-hundred kg each of separate materials having 400 ppm eU and 800 ppm eTh respectively were required. The uranium material was to be prepared by CCRMP at CANMET by silica dilution of BL-5, a CCRMP uranium ore which had been certified for both its uranium and radium content. The Resource Geophysics and Geochemistry Division of GSC undertook to search for a suitable thorium-bearing material, to be similarly diluted by CCRMP if required. The eTh/eU of this material was required to be a minimum of about 100.

Initially, thorium-bearing material was collected from a carbonatite located by an airborne gamma-ray survey over Algonquin Park, Ontario. Preliminary gamma-ray analyses of several hand samples indicated an equivalent thorium content of about 1000 ppm and an eTh/eU in excess of 100. However, following subsequent crushing and grinding, the eTh/eU was found to be only about 50. Evidently uranium-rich material was present despite the similar appearance of individual samples. Because of this variability in the eTh/eU ratio, and the difficulty of obtaining the large amount of material required, other potential sources for the thorium standard were investigated.

In June 1984, material was collected from a britholite vein associated with the Oka carbonatite near Montreal, Quebec (6,7). This particular source was selected on the basis of the previous analyses by GSC shown in Table 1 (7). Samples of the britholite vein were hand-selected from a partly-filled trench on the basis of their high radioactivity as measured with a scintillometer. The massive, fine-grained steely-grey material had a density of about 4 gm/cc. Fine-grained mica and magnetite were apparent. At a few locations, the material was quite micaceous. About 100 kg was collected, with individual pieces ranging from 0.1 to 2 kg.

Because of the variability of the Algonquin carbonatite, it was considered necessary to measure the eTh/eU in a significant fraction of the britholite samples before they were crushed and blended to ensure that the final material would meet the required eTh/eU value of 100. Sodium-iodide gamma-ray spectrometry was found to be unsuitable for this test because of interferences between the thorium and uranium spectra which resulted in a large uncertainty in the uranium concentration and associated eTh/eU ratio.

This report describes the development and application of a method for the rapid analysis of the eTh/eU ratio in whole rock samples of this material using the high resolution gamma-ray spectrometry facility of MSL, CANMET.

EXPERIMENTAL

PRINCIPLES

Thallium-208 (thorium decay series) and bismuth-214 (uranium-238 decay series) emit gamma-rays at 583.2 and 609.3 keV respectively (8,9). With high resolution gamma-ray spectrometry the two gamma-rays can be measured independently.

The measured photopeak intensity depends on the concentration of the individual isotope, the source-detector geometry and the gamma-ray attenuation properties of the source. However, because of their similar energies, the ratio (G) of the photopeak intensity of the thallium peak to that of the bismuth peak will only depend on the concentrations of the two isotopes. The only requirement is that the thallium and bismuth be distributed similarly in the source material. The measured equivalent thorium to equivalent uranium ratio (R) is then proportional to G, i.e.

$$R = KG$$

where the constant K can be obtained from measurements on a uranium-thorium ore of known concentrations.

GAMMA-RAY MEASUREMENTS

Gamma-ray measurements were performed with a high purity germanium coaxial crystal spectrometer (APTEC/NRD CS10-A31c), contained in a 10 cm thick lead castle. Rock samples (0.1 to 2 kg) were placed on a 0.25 mm steel support mounted directly on the end window for counting. The crystal has an active volume of 56 cm^3 and a 0.5 mm thick Al window and a rated efficiency of about 12% relative to a 3x3" NaI crystal at 1.33 MeV. A Canberra Series 85 multichannel analyser system was used for data acquisition from 0 to 1.48 MeV. Energy calibration corresponded to 0.1772 keV/channel. The measured full widths at half-maxima of the photopeaks

near 600 keV were 1.2 ± 0.1 keV. Photopeak areas (A) were measured over 3.4 and 4.0 keV (19 and 22 channel) intervals respectively for ^{208}Tl and ^{214}Bi, corresponding to 99.9% of the Gaussian component areas. Linear background stripping was carried out by measuring the Compton (and any peak tailing) contributions over 1.77 keV (10 channel) intervals adjoining both sides of a photopeak,

$$A = I - (N/20)B,$$

where I is the total counts in the photopeak and background intervals, B is the sum of counts in the background intervals, and N the total number of photopeak and background channels. The uncertainty in A due to counting statistics is:

$$\sigma A = [I + (N/20)^2 B]^{\frac{1}{2}}$$

Ambient background photopeak count rates were found to be 0.01 ± 0.01 s^{-1} (^{208}Tl) and (5.5 ± 3.6)x10^{-4} cps (^{214}Bi), and where these represented significant contributions, corrections were applied.

It is important to assess the uncertainty in the measured value of eTh/eU, R, where

$$R = KA_{Tl}/A_{Bi}$$

In the present experiments where low ^{214}Bi activities are measured for short counting periods, the uncertainty in A_{Bi} predominates in determining the uncertainty in R, and the relatively minor uncertainties in K and A_{Tl} may be neglected. Furthermore, since the uncertainties in the A_{Bi} are large e.g. Table 5, statistical error propagation formulae (based on σA A) are not useful to estimate the uncertainty in R. A minimum value of R (R^-) at a given probability can be found by substituting the maximum probable value for A_{Bi} (at the corresponding confidence level) in the equation for R:

$$R^- = KA_{Tl}/(A_{Bi} + m.\sigma A_{Bi})$$

where m can be calculated from the Gaussian probability distribution (10).

CALIBRATION

The calibration of the equipment was performed using CCRMP certified uranium/thorium reference ores DH-1a and DH-1 (11) to convert the ratio of the photopeak areas to eTh/eU. These particular materials were selected for calibration because the uranium and thorium concentrations are sufficiently high that both photopeak areas could be measured reliably. The gamma-ray spectrum of DH-1 is illustrated in Figure 1. The relevant photopeaks at 583 keV (^{208}Tl) and 609 keV (^{214}bi) are well-resolved and free from interferences from other gamma-ray peaks. A minor photopeak at 580 keV from ^{214}Pb in the uranium decay series interferes with the low-energy side background measurement for ^{208}Tl for both DH-1 and DH-1a (Figure 1, expanded scale). For these materials, the background was extrapolated from the high-energy side. For materials having eTh/eU 1, the interference can be neglected.

The calibration results used to derive the factor K for converting the photopeak ratio to eTh/eU are compiled in Table 2. The emanation rates of ^{222}Rn from DH-1 and DH-1a of 4% and 5% respectively were applied in calculating K (17). As expected, K was found to be independent of the source material or geometry.

Results of tests of the calibration are compiled in Table 3. The test samples were thorium-rich reference materials exhibiting a range of thorium to uranium ratios which were measured "as is" in bottles. With the exception of the thorium nitrate, concentrations were taken from the literature and, where unavailable, uncertainties were estimated as one unit in the last significant digit (12-14). The thorium nitrate sample, from Amersham Corp. and prepared in 1906, was analysed chemically at CANMET and found to contain 40.75 ± 0.05% thorium. The equivalent uranium content of this sample was calculated from reported values for ^{226}Ra and ^{210}Po activities (1). ^{226}Ra has been found to be in secular equilibrium with ^{238}U in DL-1a (4). For the syenite rock material, SY-3, and silica-diluted monazite, NBL-106, secular equilibrium was assumed. Hence, Th/U is equal to eTh/eU for DL-1a, NBL-106 and SY-3. The gamma-ray spectra of the 1906 thorium nitrate and the New Brunswick Laboratory reference material NBL-106 are illustrated in Figures 2 and 3 respectively. From Table 3 it is seen that the gamma-ray values for eTh/eU are in fairly good agreement with the calculated values despite considerable variations in the isotope activities and counting geometries.

SAMPLING TIME

Spectra of a britholite rock sample accumulated for different lengths of time are compared in Figures 4 and 5. The effect of counting statistics is apparent in the point-scatter of the 120 s measurement, nontheless useful information is obtained. The $^{208}Tl/^{214}Bi$ intensity ratio is 34.6 ± 2.6 for the 9600 s measurement and 31 (+47,-12) for the 120 s measurement.

The results of the rapid method of analysis performed on several thorium-rich materials are shown in Table 4, where repeated measurements were made for 120 s counting periods. Means of the replicate values for eTh/eU are in agreement with the more precise values obtained with long counting times. Precisions of the eTh/eU ratio values obtained with 120 s measurements are indicated by the ranges of these values and the relative standard deviations of individual measurements from the means. The samples with eTh/eU ratios considerably below 100 are readily detected in single measurements of this duration. Those samples having eTh/eU ratios considerably above 100 are also invariably identified as being acceptable in single measurements, since the relatively large measurement uncertainties are not so large as to permit values below 100. When eTh/eU approaches 100, as illustrated by the 139 g britholite sample, the precision of the measured value is about 15-20% (RSD). Acceptance of a small percentage of samples having measured eTh/eU ratios of 100 or somewhat lower would be unlikely to seriously compromise the final blended product provided that the uranium was not preferentially concentrated in these samples. Measurement periods of 60-300 seconds were therefore applied in analysing the Oka britholite samples.

RESULTS AND DISCUSSION

The results of the eTh/eU analyses of the britholite rock samples are shown in Table 5. The samples represent about 10% of the collected mass. With two exceptions, measured values of eTh/eU exceed 100, although about 60% of the samples had values in the range 100-150. Owing to counting uncertainties, precisely-determined values for some of these would

conceivably be found to be below 100. The estimates of the minimum possible values (at the 90% confidence level) for the eTh/eU ratios are shown in the table. The estimated probability that the samples in fact exceed 100 are also shown.

The eTh/eU, R_T, ratio of the final material depends on the eTh/eU ratio of the component samples, their individual masses and thorium (or uranium) concentrations, as outlined in the Appendix. Since only one sample (#6) had an eTh/eU ratio less than 100, it is reasonable to expect that the ratio obtained following crushing of all measured samples would exceed 100. A precise estimate of eTh/eU for the mixture requires a knowledge of the distribution of the thorium concentrations amongst the samples. Owing to the variable geometry of the rock samples, however, the thorium concentrations cannot be determined precisely from the gamma-ray measurements.

Nonetheless, the ^{208}Tl count rate measurements in Table 5 are not inconsistent with an approximately constant eTh concentration. The increase in the count rate of this photopeak with mass (and size) of the sample (from 60 to 100 cps) is consistant with a relatively constant eTh concentration, the increase being expected from the additional ^{208}Tl sources present as the size increases. Beyond about 700 g the count rate no longer increases, consistent with a constant eTh concentration and an effective volume limit from which unscattered ^{208}Tl gamma-rays reach the detector in significant numbers.

Based on the assumption that the eTh concentration is constant from sample to sample, the eTh/eU ratio for the final crushed material is predicted to be 132, as outlined in the Appendix. Interestingly, if it is alternatively hypothesized that the ^{208}Tl count rate is proportional to the eTh concentration (i.e. that the limiting volume of significant contributors of the detected photopeak radiation is present in all samples), then the eTh/eU ratio is also found to be 132. Neither result differs significantly from the value of 146 predicted by computing the mass-weighted average of the sample R_i's.

On the basis of the measurements and these theoretical interpretations, it was concluded that the eTh/eU ratio of the final material would exceed 100, reasonably assuming that the 10% sampling was probably representative.

ANALYSIS OF THE CRUSHED MATERIAL

The britholite samples were crushed, to approximately -100 μm. Gamma-ray spectrometry measurements of the concentrations of eTh and eU (%) were made on this material. Tared samples were packed to fill standard geometry thin steel cans that were sealed and mounted directly on the end window of the detector assembly. Cans remained sealed for three weeks prior to the final measurements to ensure that $^{214}Bi/^{226}Ra$ ratio had reached secular equilibrium. The CCRMP reference material DH-1a (0.091 ± 0.003% Th and 0.2629 ± 0.003% U) was similarly canned and used for calibration (11). Photopeaks at 583 keV (^{208}Tl), 911 keV (^{228}Ac), and 609 keV (^{214}Bi) were used in the analysis of the final material. A $^{125}Sb/^{154}Eu$ point source (NBS-4275) was used to measure and correct for relative absorption differences between the sample and standard. The effect of sample self-absorption was calculated as:

$$A(\text{corrected}) = A(\text{measured}) \times S,$$

where

$$S = -\text{Ln}(T/T_0)/(1-T/T_0)$$

and T and T_0 are the photopeak areas of a transmission source emission of similar energy when mounted on top of the canned sample and empty can respectively (15,16). The transmission source lines at 600.6 keV were used to correct the 583 and 609 keV measurements, and lines at 873.2 and 1004.8 keV were used to correct the 911 keV measurement.

The gamma-ray measurement data for the Oka britholite and DH-1a calibration material are presented in Tables 6 and 7. To avoid possible drift effect, the calibration run made on the same day was applied to compute eTh and eU. This required small corrections for the known ^{222}Rn emanation rate of DH-1a of 5.5 ± 2% (17), i.e. %eU = 0.950 (%U), %eU = 0.971 (%U), and %eU = 0.999 (%U) for the 0.5, 3.5 and 21.6 d calibrations respectively. The relative self-absorption correction factors, arising largely from the higher density of the britholite sample than the DH-1a standard are about 1.05 and 1.03 for measurements in the regions of 600 keV and 900 keV, respectively (Table 7).

The gamma-ray results for eTh and eU in the Oka britholite obtained at different intervals following sealing are compiled in Table 8. Since neither eTh or eU increase significantly with time after sealing, it is inferred that emanation of both thoron and radon is insignificant. The crushed material was found to contain 2.74 ± 0.11% eTh and 0.0283 ± 0.0010% eU for an eTh/eU ratio of 97 ± 3.

CONCLUSION

A -100 µm powdered thorium ore having an equivalent thorium to equivalent uranium ratio suitable for calibration of the thorium response of gamma-ray spectrometers was obtained by crushing of the Oka britholite material.

The eTh/eU ratio obtained in this material was actually somewhat lower than predicted from the analysis of this ratio in 10% of the source rock material, consisting of randomly selected samples. It is apparent that there were one or more equivalent uranium-rich specimens amongst the unmeasured samples that were subsequently crushed. There was however no indication of the potential for the presence of such low-grade material from the sample measurements, and further testing was therefore deemed unnecessary.

The measured eTh/eU ratio of 97 represents a factor of 3.5 increase over that available in silica-diluted monazite reference materials from the New Brunswick Laboratory.

It is intended that the Oka material will be homogenized and diluted with non-radiogenic silica to provide a 'rock-grade' gamma-ray calibration material of 800 ppm eTh to be made available through the International Atomic Energy Agency.

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Table 1 - Analysis of specimen of Oka britholite previously acquired by GSC (7)

Component	Concentration %
R.E. Oxides	33.43
CaO	28.84
P_2O_5	16.96
SiO_2	12.28
ThO_2	5.62
F	2.10
H_2O	0.54
Al_2O_3	0.47
Na_2O	0.21
MgO	0.20
Fe_2O_3	0.14
TiO_2	0.09

Table 2 - Calibration of ^{208}Tl to ^{214}Bi gamma-ray photopeak ratio using CCRMP reference materials

SRM	Configuration	eTh/eU	A_{Tl} (2σ%)	A_{Bi} (2σ%)	K*(±2σ)
DH-1a	40.5 g, sealed 21 d	0.346	16106 (2.3)	194661 (0.5)	4.18±0.10
	40.5 g, sealed 3 d	0.355	40892 (1.4)	485133 (0.4)	4.21±0.06
	40.5 g, sealed 2 h	0.364	28283 (1.7)	321360 (0.4)	4.14±0.07
DH-1a	Bottle, ≈200 g	0.364	10987 (2.7)	121428 (0.6)	4.03±0.11
DH-1	Bottle, ≈130 g	0.612	14079 (2.3)	98086 (0.7)	4.26±0.10
			23542 (1.7)	155140 (0.5)	4.03±0.07
			Mean (RSD%):		4.14 (2.3)

*K is the factor required to convert the intensity ratio, A_{Tl}/A_{Bi}, to the concentration ratio, eTh/eU.

Table 3 - Measured values for eTh/eU in reference materials

Material	% Th	%U	Th/U[1]	Geometry	Time (ks)	Area (±2σ%)		eTh/eU Found	Precision (95% CI Range)
						^{208}Tl	^{214}Bi		
DL-1a	0.0076	0.0016	0.66±0.04	200 g, 8 oz bottle	60	4856 (13)	29864 (1.2)	0.68	0.55-0.77
SY-3	0.099	0.065	1.52±0.04	109 g, 4 oz bottle	30	25063 (2.1)	77332 (0.9)	1.36	1.30-1.38
NBL-106	1.00	0.035	28.6 ±1.1	130 g, 3x602 bottle	2.2	21932 (1.5)	3827 (5.7)	23.7	22.1-25.5
Aged thorium nitrate	40.75	0.052[2]	783±29	~8 g, plastic vial	10	534464 (0.4)	3928 (23)	563.	456 -734
					10	478841 (0.4)	3180 (28)	624.	485 -869

1. Last digit in published concentrations was assumed uncertain, unless other information was available.
2. Equivalent uranium from ^{226}Ra and ^{210}Po measurements (1).

Table 4 - Effect of counting statistics on eTh/eU obtained with brief measurement periods

Material	Mass (g), Geometry	Time (s)	Number Measurements	Mean Photopeak Area (RSD%)		eTh/eU Found				
				^{208}Tl	^{214}Bi	Range	Mean	RSD(%)	Long Count Value(ks)	
NBL 106	150, bottled	120	10	1227 (3.3)	224 (7.0)	20.1-25.5	23.3	7.5	23.7±2.0	(2.2)
Oka Britholite	139, chunk	120	10	4994 (1.5)	173 (20)	89 -165	132.	21.	140 ±13	(5.1)
		120	5	5095 (1.8)	176 (14)	108 -168	122.	17.		
Oka Britholite*	408, chunk	120	9	10528 (1.2)	160 (28)	187 -560	297.	37.	268 ±18	(30)
Aged thorium nitrate	8, vial	120	7**	6127 (1.4)	56 (50)	229 - ∞	527.	-	594 ±130	(10)
		300	5	16168 (0.6)	132 (74)	265 -5000	1444.	140.		
		600	10	28746 (1.1)	180 (52)	294 -2393	877.	67.		
		1376	1	65934 (-)	492		555.			
		5332	1	255610 (-)	1727		613.			

*GSC Reference Sample, collected previously.
**Three additional runs gave negative values for the ^{214}Bi area

Table 5 - eTh/eU in Oka britholite source rocks (1,2)

Sample No.	Mass (g)	Count Time(s)	Photopeak Count Rate				eTh/eU		
			^{208}Tl		^{214}Bi		Found	Minimum (90% Confidence Level)	Probability, % [eTh/eU 100]
			s^{-1}	(2σ, %)	s^{-1}	(2σ, %)			
16	70	202	59.2	(2.2)	1.49	(53)	166	124	99
3	201	96	111.1	(3.0)	4.44	(42)	104	82	57
15	206	228	54.9	(2.2)	1.33	(55)	170	125	99
12	231	61	65.3	(4.3)	2.02	(78)	134	89	81
		206	65.8	(2.1)	1.62	(53)	168	125	99
		2091	64.3	(0.7)	1.56	(14)	171	157	99
5	309	74	68.5	(3.9)	2.74	(57)	103	75	54
13	313	183	81.5	(2.2)	1.61	(64)	210	149	99
4	409	157	85.9	(2.3)	0.84	(165)	422	204	99
		266	85.7	(1.8)	1.37	(65)	259	183	99
6	447	66	72.0	(4.2)	3.14	(55)	95	70	43
11	480	150	83.1	(2.5)	2.51	(49)	137	104	93
18	491	134	68.1	(2.8)	2.01	(54)	140	104	93
2	548	68	82.1	(4.0)	3.34	(58)	102	74	52
17	640	92	78.2	(3.5)	2.51	(61)	129	93	83
14	690	266	110.9	(2.1)	1.16	(107)	396	235	99
8	1111	91	101.9	(3.3)	3.87	(51)	109	87	64
9	1171	108	94.1	(3.0)	3.04	(56)	128	94	84
10	1442	115	104.3	(2.9)	3.63	(54)	118	88	75
1	1942	161	95.4	(2.7)	3.39	(49)	117	89	75
		131	99.5	(2.8)	3.59	(50)	115	87	73
7	2200	62	98.5	(4.4)	2.79	(93)	146	91	84

1. Estimates for eTh/eU of the homogeneous blend of these samples, R_T:
   a) $R_T = (\Sigma W_i R_i)/\Sigma W_i = 146$, "weighted-mean" estimates;
   b) $R_T = (\Sigma W_i)/(\Sigma W_i/R_i) = 132$, constant thorium concentration hypothesis;
   c) $R_T = (\Sigma C_i W_i)/(\Sigma C_i W_i/R_i) = 132$, assuming that the ^{208}Tl count rate is proportional to C_i;
   where W_i, C_i and R_i are respectively the mass, thorium concentration and eTh/eU ratio of the ith sample. Refer to Appendix for derivation of relationships.

2. Replicate measurements of samples 1 and 4 were made with different faces of the samples towards the detector.

Table 6 - Gamma-ray measurement data, crushed material

Sample	Geometry	Time Sealed (d)	Count Time (ks)	Photopeak Area (±2σ%) cps		
			KEV:	583	911	609
			ISOT:	^{208}Tl	^{228}Ac	^{214}Bi
DH-1a	40.51 g/29 mL can	0.5	42.2	0.671 (1.7)	0.398 (3.0)	7.621 (0.35)
		3.5	61.4	0.666 (1.5)	0.388 (2.5)	7.904 (0.35)
		21.6	24.0	0.671 (2.3)	0.380 (4.2)	8.110 (0.45)
		105.	24.6	0.690 (2.3)	0.391 (4.0)	8.25 (0.45)
Oka Britholite	56.75 g/29 mL can	0.2	20.0	26.51 (0.35)	16.20 (0.35)	1.13 (4.3)
		3.8	22.4	26.87 (0.35)	16.46 (0.35)	1.16 (3.9)
		22.	55.7	26.33 (0.15)	16.04 (0.25)	1.18 (2.4)
		104.	56.2	26.75 (0.15)	16.33 (0.25)	1.19 (2.4)

Table 7 - Gamma-ray absorption measurement data

Sample	Photopeak Area (±2σ%) cps			Absorption Correction Factors		
	KEV:	601+607	873	1005			
	ISOT:	^{125}Sb	^{154}Eu	^{154}Eu	601+607	873	1005
DH-1a	31.0 (1.7)	20.4 (1.1)	27.2 (1.0)	1.16±.01	1.122±.007	1.122±.006
Oka Britholite	27.6 (1.8)	19.2 (1.0)	25.7 (1.0)	1.22±.01	1.156±.007	1.152±.006
Empty Can	41.9 (0.9)	25.8 (0.7)	34.4 (0.6)			

Table 8 - Analytical values for blended Oka britholite powder. Calibration reference material for the gamma-ray measurements is DH-1a. Uncertainties incorporate those from counting statistics.

Period Sealed (d)	eTh, % (±2σ)		eU, % (±2σ)	eTh/eU
	583 KeV	911 Kev		
0.2	2.70±0.06	2.72±0.08	0.0278±0.0014	97.5
3.8	2.76±0.05	2.83±0.08	0.0281±0.0012	99.5
22.	2.68±0.07	2.82±0.12	0.0287±0.0008	95.8
108.	2.65±0.07	2.79±0.11	0.0285±0.0008	95.4
Mean (±95% CI):	2.74 ± 0.06		0.0283±0.0007	97.0±3.0

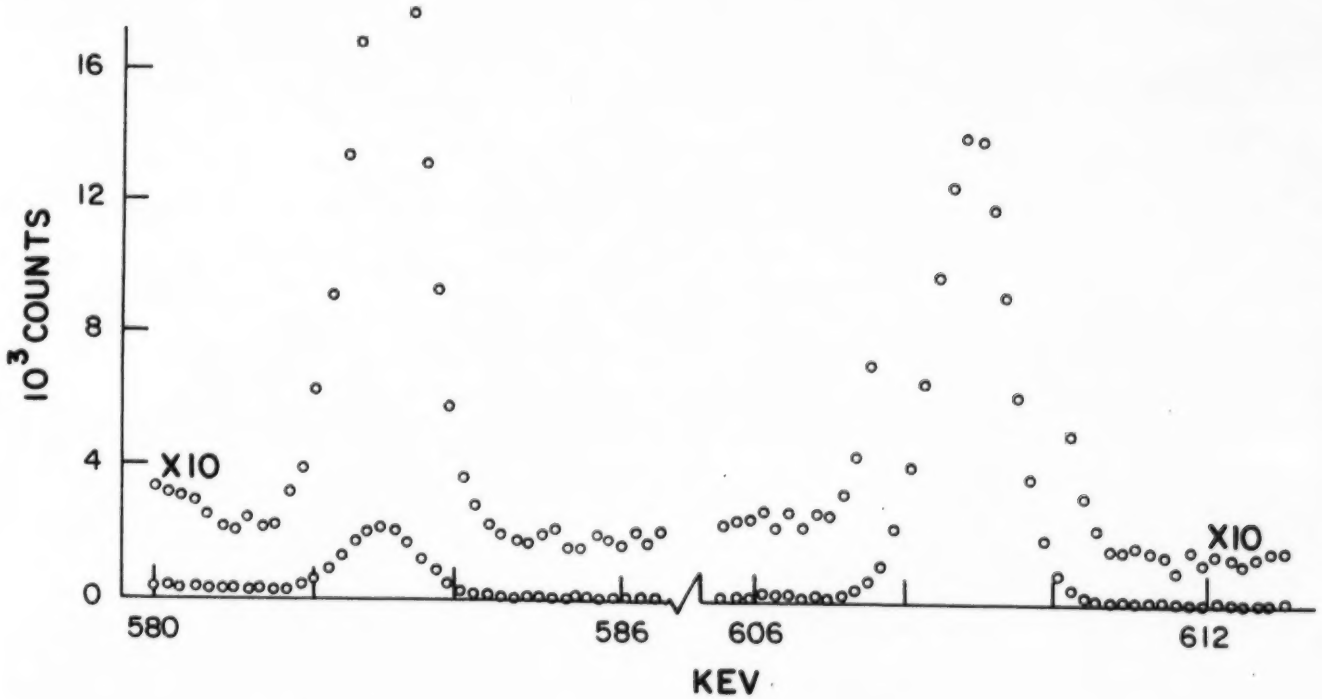

Fig. 1 - CCRMP reference material DH-1, 130 g in 8 oz glass bottle. Thorium is 0.104 ± 0.0045% and uranium is 0.177 ± 0.003% (95% CL uncertainties). Photopeak areas (±2σ%) are 13427 (2.8) and 98086 (0.7). Collection time is 12.94 ks.

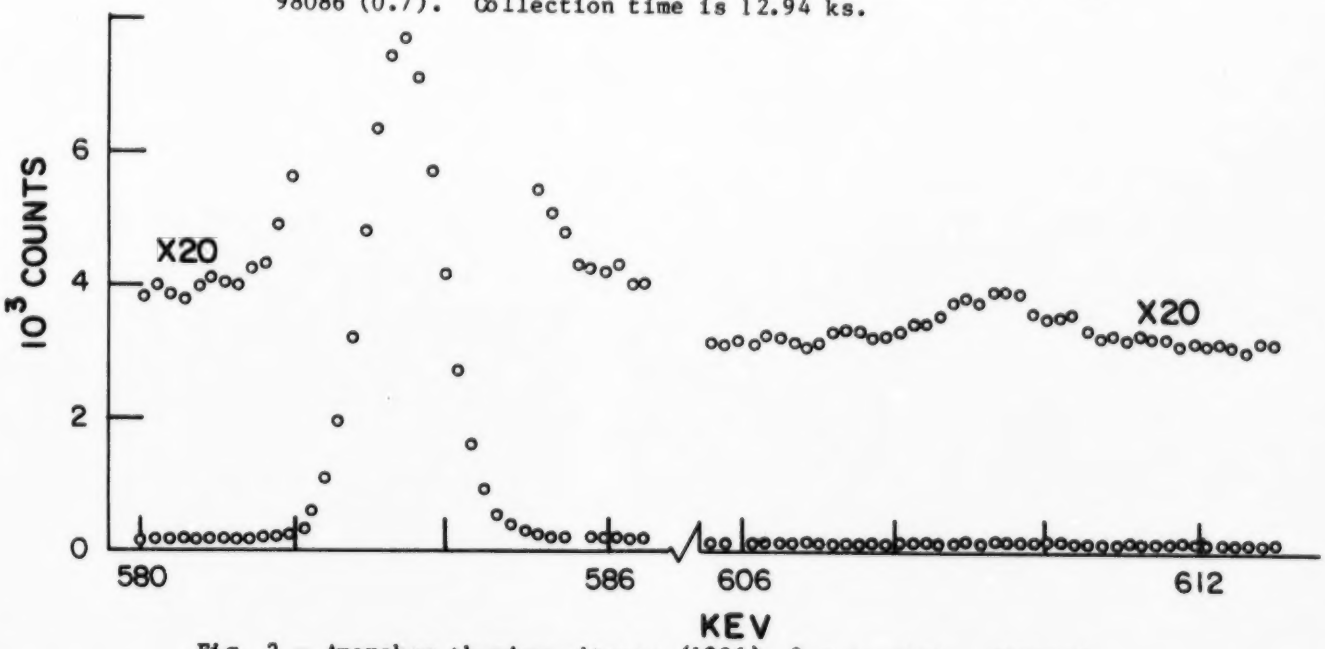

Fig. 2 - Amersham thorium nitrate (1906), 8 g in vial. Nominal eTh/eU=770. Photopeak areas (±2σ%) are 534500 (0.4) and 3934 (23). Collection time is 10 ks.

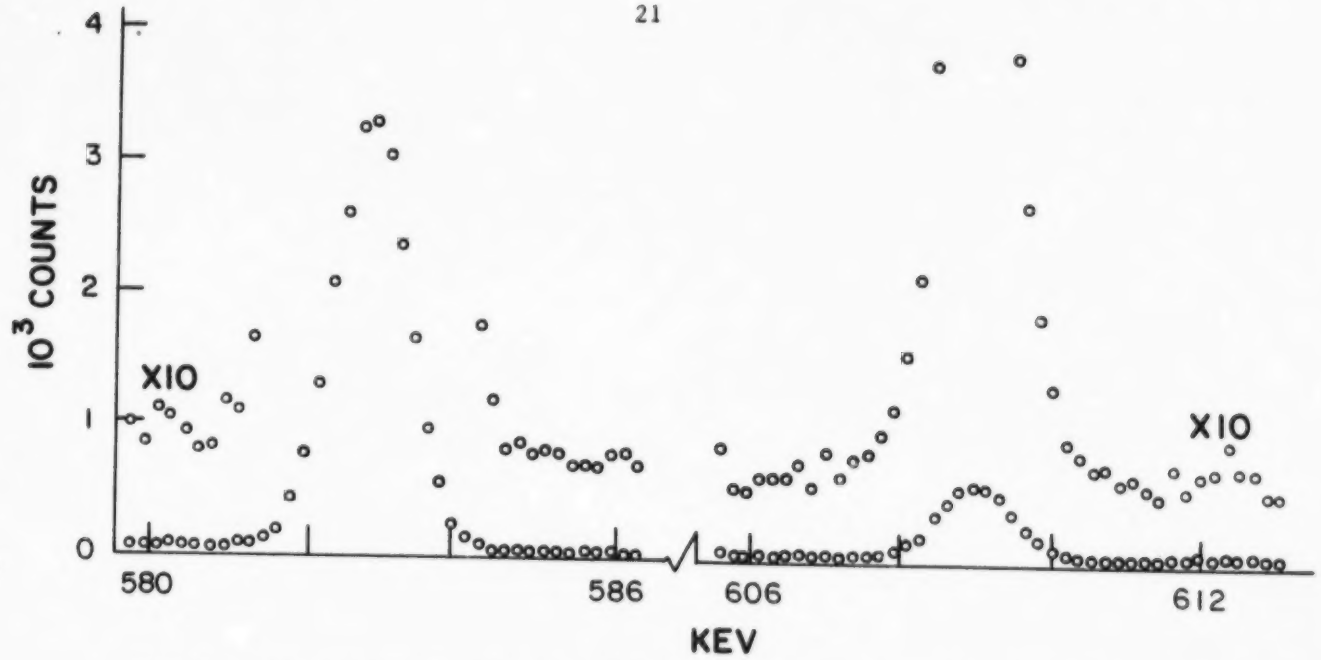

Fig. 3 - NBL reference material 106, silica diluted monazite, 150 g in three 4 oz bottles. Thorium and uranium are respectively 1.00 and 0.035%. Photopeak areas (±2σ%) are 2195 (1.5) and 3828 (5.7). Collection time is 2.2 ks.

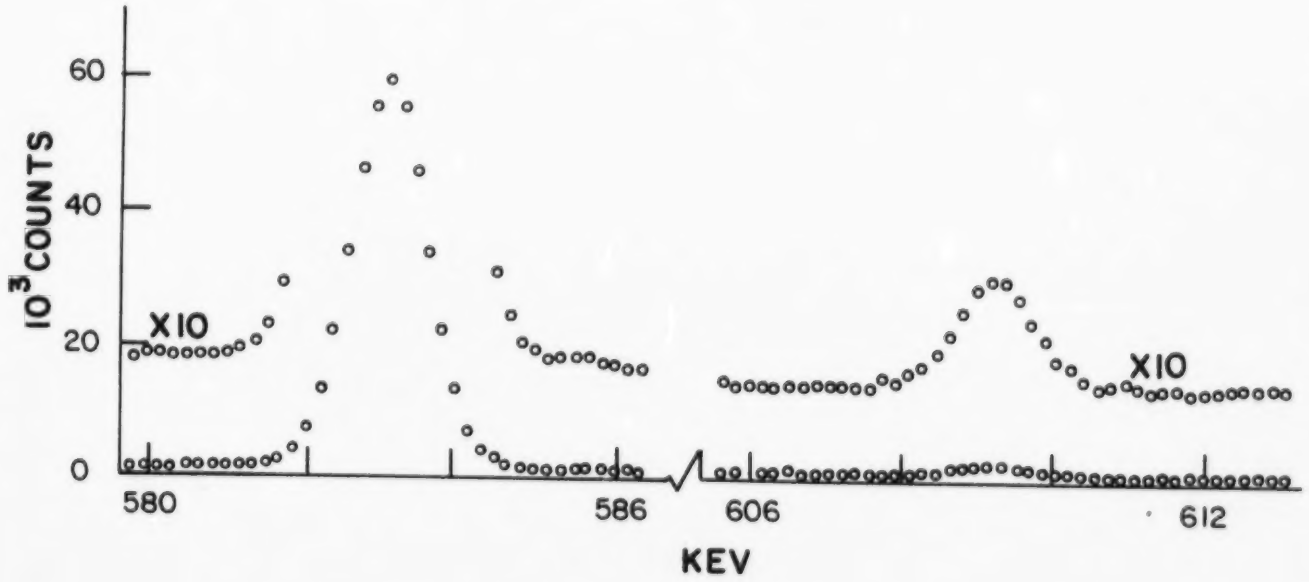

Fig. 4 - Collected specimen of rock from britholite vein, Defresne property, Oka, Quebec. Mass is 159 g. Photopeak areas (±2σ%) are 402724 (0.35) and 11761 (7.5). Collection time is 9.6 ks.

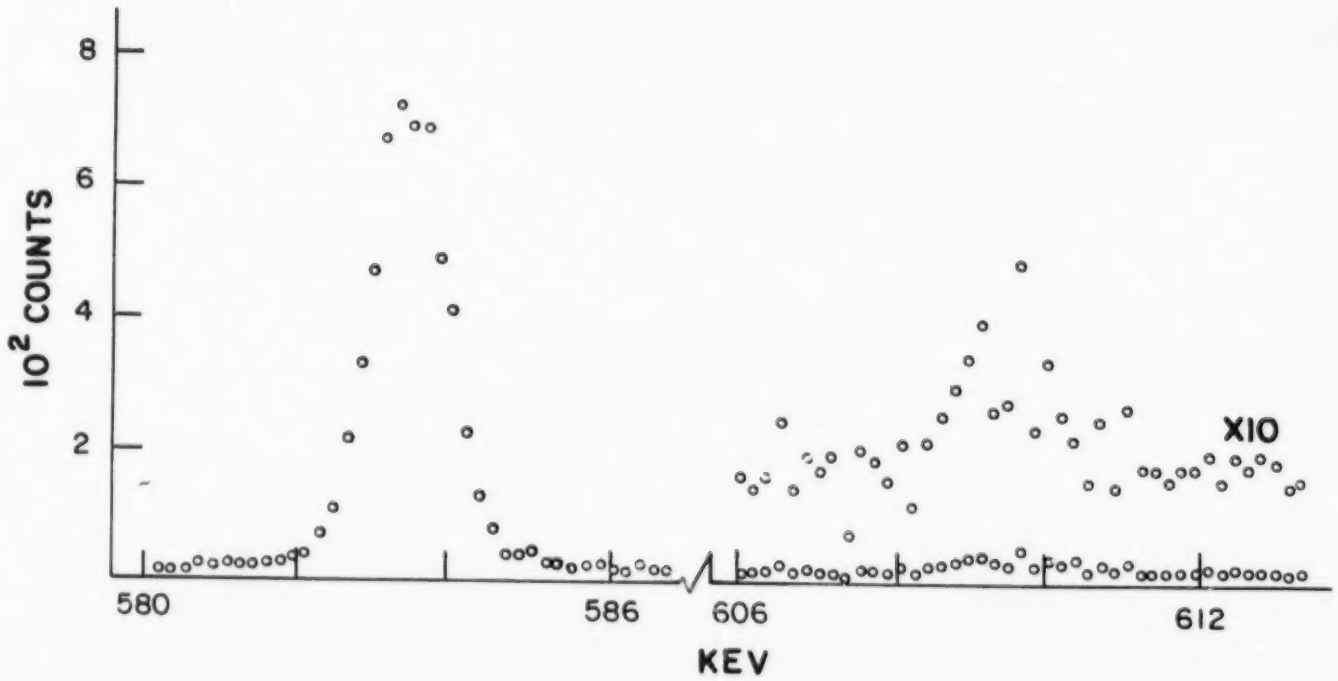

Fig. 5 - Specimen of Fig. 4, collection time 120 s. Photopeak areas (±2σ%) are 5061 (3.4) and 162 (59).

APPENDIX

Relationship between equivalent thorium to equivalent uranium ratios in the individual samples (R_i) and the ratio in the blended product of these samples (R_T).

The concentrations of thorium (C_T) and uranium (C_u) in the blended material are given by:

$$C_T = \sum_i^n (C_T)_i \; W_i / \sum_i^n W_i, \qquad (1)$$

and

$$C_u = \sum_i^n (C_u)_i \; W_i / \sum_i^n W_i \qquad (2)$$

where $(C_T)_i$ and $(C_u)_i$ are the concentrations of thorium and uranium in the collection of n samples each having mass, W_i.

The eTh/eU ratio of the blended material is:

$$R_T = C_T/C_u = \sum_i^n (C_T)_i \; W_i / \sum_i^n (C_u)_i \; W_i \qquad (3)$$

The uranium concentration is an individual sample can be expressed as:

$$(C_u)_i = (C_T)_i / R_i \qquad (4)$$

which, on substitution into (3) yields:

$$R_T = \sum_i^n (C_T)_i \; W_i / \sum_i^n (C_T)_i \; W_i / R_i \qquad (5)$$

If R_{min} is the minimum value of R_i for the collection of samples, then

$$\sum_i^n (C_T)_i \; W_i / R_i \geq (1/R_{min}) \sum_i^n (C_T)_i \; W_i \qquad (6)$$

Substitution of inequality (6) into (5) yields

$$R_T \geq R_{min} \tag{7}$$

Similarly, if R_{max} is the maximum value of R_i for the collection of samples

$$R_T \leq R_{max} \tag{8}$$

A range can therefore be placed on R_T defined by the minimum and maximum values of R_i in the collection. If it is required that R_T exceed some critical value, R_c, this can be ensured by eliminating samples having R_i R_c from the collection to be blended. This is the basis of the screening test.

If the special circumstance arises that variations in R_i are primarily due to variations in the uranium concentrations $(C_u)_i$ while the thorium concentrations $(C_T)_i$ remain approximately constant, then it is possible to estimate R_T from the R_i and masses, W_i, of the samples, since equation (5) reduces to:

$$R_T \doteq 1/\sum_i^n X_i/R_i \tag{9}$$

where the X_i are the weight fractions of the individual samples. This circumstance would arise if the samples are from a thorium mineral vein of essentially constant major-component composition, but containing variable inclusions of uranium-bearing minerals at trace or very minor levels. This was hypothesized in order to compare a predicted R_T to that actually obtained.

If, on the other hand both $(C_u)_i$ and $(C_T)_i$ vary considerably from sample to sample, we may only predict the range given by equations (7) and (8) since we have no a prior knowledge of the values of $(C_T)_i$ for use in equation (5).